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**Formation of Porous Clay Ceramic Using Sago Waste Ash as a Prospective Additive Material with Controllable Milling****H. Aripin<sup>1\*)</sup>, S. Mitsudo<sup>2</sup>, B. Rahmat<sup>1</sup>, S. Tani<sup>2</sup>, K. Sako<sup>2</sup>, Y. Fujii<sup>2</sup>, K. Kikuchi<sup>3</sup>, T. Saito<sup>2</sup>, T. Idehara<sup>2</sup>, S. Sabchevski<sup>4</sup>**<sup>1</sup>Research Center for Material Processing and Renewable Energy, Siliwangi University, Jl. Siliwangi 24, Tasikmalaya 46115, Indonesia<sup>2</sup>Research Center for Development of Far Infrared Region, University of Fukui, Bunkyo 3-9-1 Fukui 910-8507, Japan<sup>3</sup>Department of Applied Physics, Faculty of Engineering, University of Fukui, Bunkyo 3-9-1 Fukui 910-8507, Japan<sup>4</sup>Lab. Plasma Physics and Engineering, Institute of Electronics of the Bulgarian Academy of Sciences and Association EURATOM-INRNE, 72 Tzarigradsko Shose Blvd., Sofia 1784, Bulgaria.**Abstract:**

*A novel type of ceramic material was produced by mixing sago waste ash from the sago processing industry in Indonesia with clay. The composition was prepared by adding 50 %wt amount of sago waste into the clay, then a series of samples was milled for 6 h, 12 h, 24 h and 48 h, respectively. The samples were dry pressed and sintered at temperatures ranging from 800°C to 1200°C. The influence of the sintering temperature and the milling time on bulk density, firing shrinkage, water adsorption, and hardness was studied in detail. The results demonstrate that the low water absorption of less than 0.5% and the highest hardness of 5.82 GPa were obtained for the sample sintered at 1100°C and milled for 48 h. The investigation of the absorptive properties of such ceramics indicates that they could be recommended as a promising material for manufacturing of unglazed floor tiles.*

**Keywords:** Unglazed ceramic tile, Sago waste, Clay, Sintering temperature, Milling time, Water absorption, Hardness.

**1. Introduction**

Clay is one of the most abundant minerals and has numerous uses in various industrial applications. Among them are those related to the production of construction materials with high density and good chemical stability as, for example, in flooring and covering materials for decorative purposes (e.g. in special bricks, cements, lightweight aggregates and ceramic tiles). A promising and actively studied variety of the latter are the unglazed clay ceramic tiles that are characterized by an absence of open porosity and zero water absorption. Such advantageous parameters together with many other technological, economical and environmental benefits (easy to clean, resistant to sunlight, abrasion and chemical attack, sufficient hardness) make them a promising replacement to the commonly

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used granite, cement, wooden and plastic bricks and tiles that are widely used as floor covering.

In order to produce a high-quality unglazed ceramic tile with excellent technical characteristics the formation process requires an appropriate raw material possessing sufficient plasticity for green processing as well as an adequate degree of fluxing. As a rule, any ceramic tile is produced from a mixture that contain 80% plastic component of clay, sodium and potassium feldspar and 20% fluxes of silica and feldspar sand in an additive material [1,2]. Some of the potentially appropriate waste materials with more than 40% SiO<sub>2</sub> content can be introduced as additives into the composition used for production of sintered ceramic tiles. They include sewage sludge waste [3], blast furnace slag [4], granite sawing waste [5], tincal waste [6], borax waste [7], and cellulignin waste ash [8]. The cellulignin waste for instance can be obtained from cellulose containing biomass waste. This includes wood, sugarcane baggase, rice husk, sago, and rice straw wastes. It was found that when such waste materials are burnt, an ash with high silica content is produced. The ash can then be incorporated into vitrified clay ceramic. It should be noticed that such approach is both environmentally friendly and technologically advantageous. The porosity in the incorporated body is due to the fact that such ash includes is nano particles that form agglomerates with coarse pores. During the firing, the ash acts as a flux and contributes to the consolidation of the ceramic structure. This promotes a reduction in the water absorption and an increase in the mechanical strength. Leaching test showed that the potentially toxic metals present in the ash become inert after the ceramic firing [8]. New possibilities for utilization of cellulignin waste as additive in the ceramics producing process have also been investigated. It was found that adding waste ash and mixing it in tile slurries improves the physical properties of the tiles. The municipal solid waste (MSW) incineration bottom ash was used as an additive material in producing the clay ceramic floor tile as well [9]. The clay with 30%wt bottom ash and fired at 1125°C has a low water absorption of less than 0.5% and highest flexural strength of 75 MPa. In this case, the strength of the tile is greater than that of a standard one. The incorporation of rice husk ash in the form of silica in whiteware tile composition was investigated and an improvement in the properties with a reduction in the maturing temperature was found [10,11]. This was attributed to the sharp changes in the microstructure as a result of a significant reduction in the quartz phase content and the simultaneous increase in glass phase. In other trials, the ash from a biomass incinerator was mixed into clay body to produce a fully ceramic brick [12]. It was found that brick with 20%wt of ash meets the UNE standard compressive strength. Further, the paper processing waste were successfully used in producing the clay ceramic fired at 1200 – 1400°C [13]. The clay with 30 – 40%wt of paper waste resulted in an increase of the compressive strength from 8 to 43 MPa. These studies have demonstrated that the performance of ceramic body is strongly dependent on the favorable effects of the water absorption and fired strength.

Another important aspect of the fabrication technology which affects the quality of the ceramic tile is the role of particle homogeneity in reducing the presence of defects in tile body. Since the particle size distribution has a significant impact on the packing efficiency usually a raw material of uniformly distributed fine particles is required. Milling methods using mechanical means are known to result in reduced particle size and increased homogeneity of the compound in the ceramic powder. A study [14] has showed that an increase in milling time of the mixture up to 5 h has improved mixing, decreased particle sizes, and yielded a less agglomerated mixture. A relative density of 94% was reached at a relatively low sintering temperature of 1600°C. Further, the other study [15] has shown that with increasing the milling time up to 48 h, the density of anorthite based porcelainised stoneware has increased too. It has also been reported that the particle sizes of the ceramic body influences significantly the technical properties of the material.

In the present investigation, we study a material that is abundant in Indonesia, namely the sago waste (starch from *Metroxylon sago* also known as sago palm), which is a by-

product from the sago processing industry and evaluate its usability as an additive material for producing unglazed clay ceramic tiles. The evaluation is based on experiments carried out in order to elucidate the influence of the basic technological parameters (milling time and sintering temperature) on the physical properties such as bulk density, water absorption, firing shrinkage and Vickers hardness. The structure of the ceramics was studied by Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD).

The rest of the paper is organized as follows. In the next section we describe the used experimental procedures and methods. The experimental results are presented and discussed in Sec. 3. In the final section we draw some conclusions.

## **2. Experimental procedure and methods**

### **2.1. Preparation of the studied ceramic samples**

Sago wastes that consist of fine and coarse “hampas” (solid residue which is left behind after the starch has been washed out) were obtained from the sago processing plant in Kendari, Indonesia while the clay was delivered from the rural area of Sindangkasih, located in Konawe Selatan, Indonesia. The materials for the samples were selected manually, cleaned and dried in an oven at a temperature of 105°C for 24 hours following the procedures described elsewhere [16]. The clay with 50 wt% of sago waste was mixed with water and then the mixture was kept for ageing under ageing for one month and stirred well with high speed stirrer before milling. Four types of samples were prepared by varying the milling time. They correspond to the milling time of 6 h, 12 h, 24 h, and 48 h, respectively. For powdering, the samples were dried in an oven at a temperature of 105°C for 24 h. The dried powder and 6 wt% distilled water were mixed and then pressed at 11 MPa using hydraulic compaction to form a cylindrical pipe with a diameter of 10 mm and a thickness of 7 mm. The samples were dried heating them to 600°C with a rate of 1.47°C/min and then were kept at a constant temperature for 2 hours in an electric furnace. The samples were sintered in the electric furnace at temperatures ranging from 800°C to 1200°C. A controlled heating rate of 2.08°C/min was maintained up to the desired temperature and the temperature was kept constant for 2 hours. The cooling was performed by a natural convection after turning the electric furnace off and leaving the sample inside.

### **2.2. Apparatus, method and procedure used in the measurement**

The linear shrinkage of the fired samples was determined comparing the diameters of the green and the sintered body. Both the density and the water absorption were determined by the Archimedes' method using distilled water. X-ray diffraction (XRD) was used to study the structure of samples sintered at different temperatures. The measurements were performed with an X-ray diffractometer (Rigaku, Japan) with filtered Cu K $\alpha$  radiation having a wavelength of 0.15418 nm. The scan angle ranges from 10° to 70°. In addition, the microstructural evolution under various sintering temperatures and milling times was examined using 6301F scanning electron microscop (SEM, JOEL, Japan). Hardness of the sintered samples was measured using a Vickers microindenter at a load of 1.96 N (300 g) applied for 15 s.

**Tab. I** Chemical analysis of sago waste ash and clay.

Major chemical constituents (wt.%)	Ash of sago waste	Clay
SiO <sub>2</sub>	68.03	60.53
Fe <sub>2</sub> O <sub>3</sub>	0.76	2.00
Al <sub>2</sub> O <sub>3</sub>	6.93	25.27
CaO	14.88	0.05
MgO	2.39	0.66
Na <sub>2</sub> O	1.35	1.38
K <sub>2</sub> O	1.35	3.73
P <sub>2</sub> O <sub>5</sub>	1.66	0.04
TiO <sub>2</sub>	0.03	0.74
SO <sub>3</sub>	2.02	-
MnO	0.65	0.01
NiO <sub>2</sub>	0.02	-
Cr <sub>2</sub> O <sub>3</sub>	0.04	0.01
LOI	-	5.37

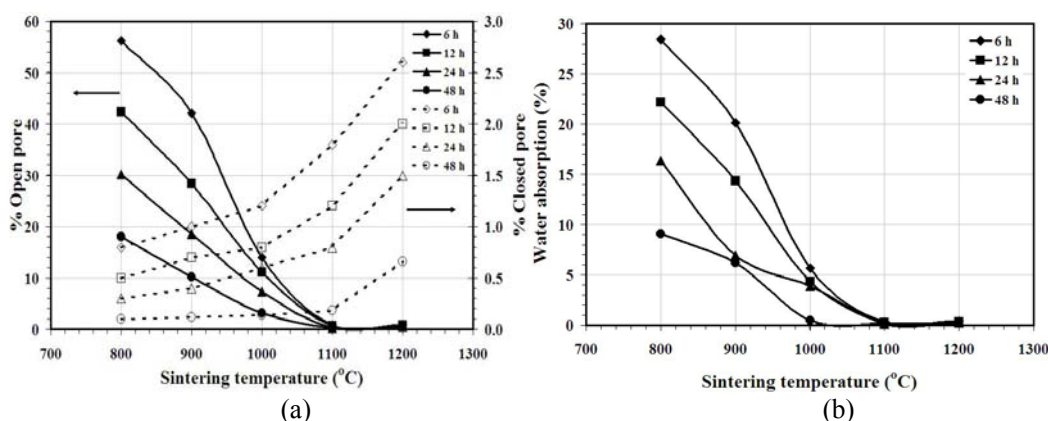
### 3. Experiment results and discussion

#### 3.1. Chemical analysis

Tab. I shows the chemical composition (oxides content) of both ashes obtained from sago waste and clay. The waste contains SiO<sub>2</sub>, CaO, and Al<sub>2</sub>O<sub>3</sub> and the clay contains SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as the main constituents. The waste and clay are rich in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, so that they have a decisive influence on the refractoriness and mechanical resistance of the ceramic tile. Those oxides of the waste are accompanied by a significant amount of CaO and MgO, which can appreciably modify the colour of the fired clay. It can also be seen that the clay and the waste contain small amount of risky oxide such as MnO. The loss on ignition is associated with the presence of clay minerals, hydroxides, organic matter and volatile components.

#### 3.2. Analysis of the technological properties

Fig. 1a shows the open and the closed pores of the sintered samples as a function of the sintering temperature which varies in the interval from 800°C to 1200°C. It is apparent that the open pores of the sintered sample decrease with increasing of the sintering temperature up to 1100°C and then slightly increases. The reason for such behavior can be explained taking into consideration a viscous liquid phase mechanism in the sintered sampel [17]. The body sample has an amorphous phase and some crystalline phases which are formed during the firing process. The amorphous phase originates from liquid clay, and it is rich in silica. Due to the presence of the surface forces created by the fine pores in the sintered sample, the liquid phase tends to fill the open pores. An increase of the temperature causes both an increase of the amount of the liquid phase and a decrease of its viscosity. As a result more pores are filled by liquid, and therefore, the number of open pores decreases, as the temperature increases from 800°C to 1100°C. Above 1100°C however, the amount of the liquid phase decreases, because it fills the large pores which volume expands due to the increased pressure of the gas inside the closed pores. Therefore, both the open and the closed pores increase.



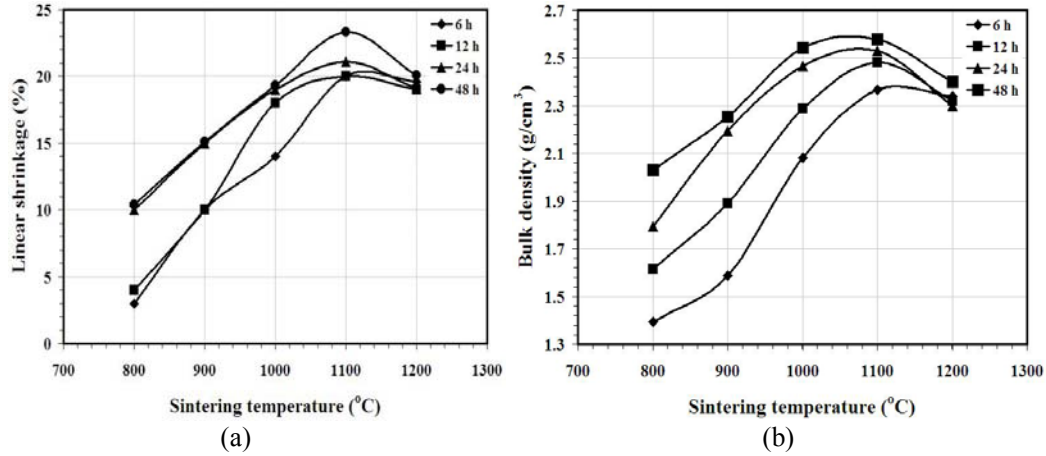
**Fig. 1.** (a) Open and closed pores and (b) water absorption of the sintered samples as a function of the sintering temperature.

It should be underlined that the open porosity decreases with increasing the milling time. According to Gnana Kumar [18], as the milling time increases, the particle size decreases to the point that there are lattice defects in the structure of the powder. By increasing the milling time from 6 h to 48 h, the amount of the porosity of the sample decreases. When the clay and sago waste mixtures were milled during shorterr time intervals rather big-sized particles of the mixture were produced. During such milling process, a little amount of fine particles fills some pores of the mixture. Thus, the packing of the mixture creates also big gaps between particles. When the mixtures were milled longer, the homogeneous powder with fine particles were produced and more pores were blocked by smaller mixture particles. Obviously, the smaller particles pack tightly and the gaps between them are narrower. Therefore in the latter case the sintering is more efficient and the open porosity is less.

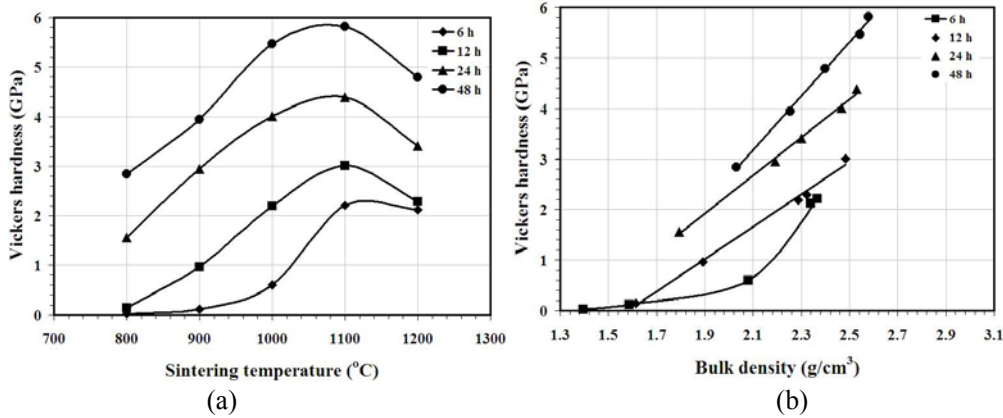
Fig. 1b shows the variation in water absorption with sintering temperature for ceramic bodies milled for different times. The water absorption is directly related to the presence of open pores, and the results show that its value decreases in the temperature range from 800 to 1100°C and slight increases above 1100°C. With increasing the milling time up to 48 h, a beneficial effect, namely a reduction of the water absorption is found. The temperature needed in order to reach a minimum water absorption level gradually decreases with increasing the milling time. The milling time of 48 h led to a reduction of the sintering temperature required for attaining a minimum water absorption by 100°C. According to ISO 13006 standard, the water absorption of less than 0.5% is needed for manufacturing of unglazed floor tiles [19]. Our experimental results show that the water absorption of the samples sintered at temperatures higher than 900°C and milled for 48 h meet the requirements of this standard.

Fig. 2 shows the linear shrinkage and the bulk density of the sintered samples as a function of the sintering temperature. It was found that the linear shrinkage increases with increasing the sintering temperature and the maximum occurs at 1100°C. The measured bulk density exhibits a similar trend as that of the linear shrinkage, i.e. initially increases, reaches a maximum value, and then decreases above 1100°C. The maximum bulk density was reached at sintering temperature of 1100°C and milling time of 48 h. The increase in the bulk density can be related to the improvement in the particle packing. The smaller size particles dispersed among larger ones can increase the powder reactivity and can produce a liquid phase, which reduces the space occupied by pores between the particles. The decrease in the bulk density above 1100°C is attributed to a pore volume expansion, which is due to an increased pressure

of gasses entrapped within the closed pores [15]. The role of pores is very important for controlling the value of the bulk density in the sintered sample.

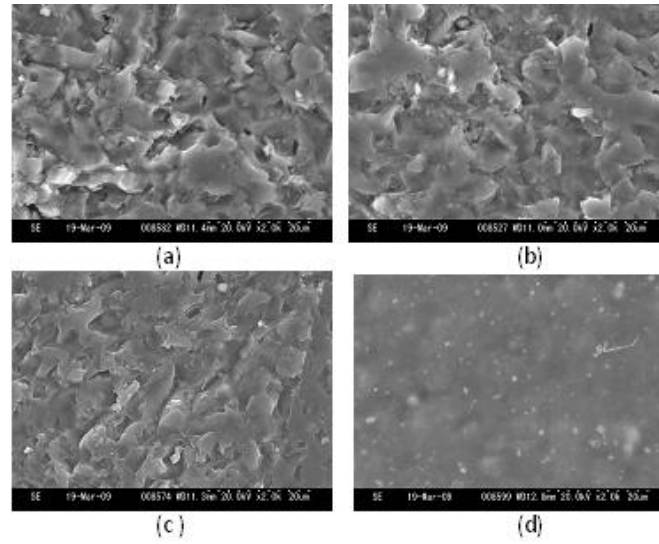


**Fig. 2.** (a) Linear shrinkage and (b) bulk density of the sintered sample as a function of the sintering temperature.

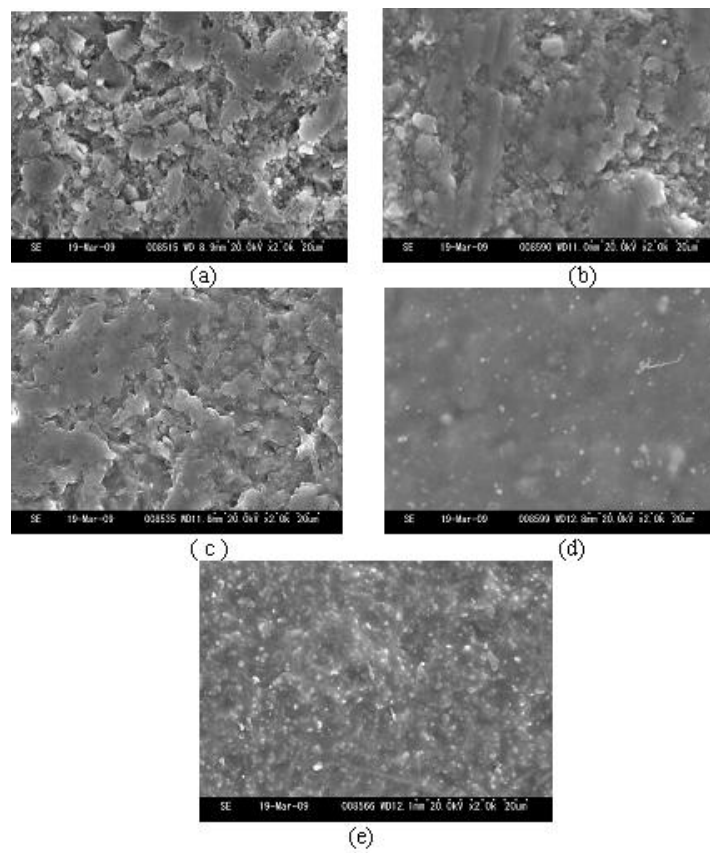


**Fig. 3.** (a) Vickers hardness of the sintered sample as a function of the sintering temperature, and (b) the relationship between the Vickers hardness and the bulk density.

Fig. 3a shows the Vickers hardness behaviour of the sintered sample as a function of the sintering temperature. It can be seen that the lowest hardness was measured for all samples sintered at 800°C, whereas the maximum hardness value was measured for all samples sintered at 1100°C. The general trend which can be observed from Fig. 3a is that the hardness increases from 800 to 1100°C, however a further increase of the temperature (values higher than 1100°C) results in its decrease. The hardness for all samples milled from 6 to 48 h and sintered from 800°C to 1200°C was higher than the minimum limit of 35 MPa for ceramic tile required by the ISO standard [19]. Fig. 3b shows the relationship between the Vickers hardness and the bulk density of the sintered samples. The Vickers hardness was found to be proportional to its bulk density, except for the sample milled for 6 h. For the samples milled for 12, 24, and 48 h, its hardness trend correlates linearly with the change in the bulk density. This means that the hardness is governed by the change of the bulk density. Further, for the sample milled for 6 h a non-linear variation of the hardness with bulk density was observed. It can be ascribed to the presence of larger grain sizes which are detrimental to the hardness of the sintered sample.



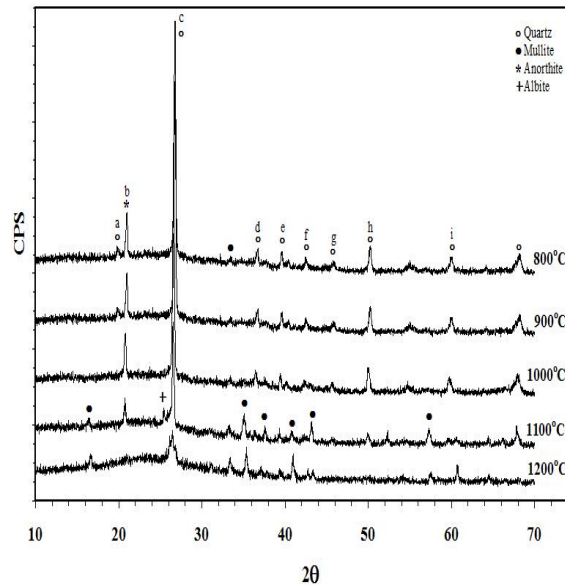
**Fig. 4.** SEM picture of the samples sintered at 1100°C and milled at (a) 6 h, (b) 12 h, (c) 24 h and (d) 48 h.



**Fig. 5.** SEM picture of the sample milled at 48 h and sintered at (a) 800°C, (b) 900°C, (c) 1000°C, (d) 1100°C and (e) 1200°C.

### 3.3. Results from a microstructure analysis

Fig. 4 shows SEM picture of the samples sintered at 1100°C and milled at different times. In the sample sintered at 1100°C and milled for 6 h, both rough surfaces and large pores can be observed. With increasing the milling time up to 48 h, the roughness and the number of pores at the surface of appear to be reduced. Fig. 5 shows SEM image of the sample sintered at different temperatures and milled for 48 h. It can be seen that their textures are similar to the images of the sample surfaces shown in Fig. 4. With increasing the temperature up to 1000°C, a clustering of particles is apparent, as a result of the incomplete filling of the pores by the liquid phase. The incorporation of the particles and the reduction of porosity in the sintered samples can be observed above 1000°C. At a temperature of 1100°C, the amount of liquid phase is larger and it fills more pores. As a result a dense layer of the sample surface is observed and pores are not seen at all. At 1200°C, a low amount of very small isolated pores is observed.



**Fig. 6.** XRD patterns of the samples milled at 48 h and sintered at different temperatures.

### 3.4. Mineralogical analysis

Fig. 6 shows XRD patterns of the samples milled for 48 h and sintered at different temperatures. It reveals that the sample sintered at 800°C consist of quartz ( $\text{SiO}_2$ ), mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). The temperature does not have any effect on the formation of crystals and the crystalline phases remain almost unchanged in the temperature range from 800°C to 1000°C. Quartz is the only mineral phase existing in the green body and detected in the sintered samples. All the other mineral phases existing in the raw materials (see Table 1) have disappeared, and actually replaced by a mullite and a glass phase. Mullite has already been formed at 800°C, as one of the minor crystalline phases and co-exists with quartz and anorthite. As the sintering temperature increases, the peak intensity of mullite increases while the other crystalline phases tend to decrease. This indicates that the increase of sintering temperature significantly changes the degree of crystallinity. With the increase of the temperature up to 1200°C, crystalline quartz gradually disappears which can be seen from



the reduction of the peaks a, c, d, e, f, g, h and i as shown in Fig. 7. Albite and mullite derived from crystalline quartz dissolution remain in the liquid phase and lead to the increase of Si-O-Si bond [20], which resulted in the enhancement of the density at 1100°C.

#### 4. Conclusion

A mixture of 50 %wt clay and sago waste, which was aged for one month has been studied as a raw material for production of unglazed clay ceramic tiles. It was found that an increase of the milling time reduces both the open and the closed pores of the sintered sample. The samples milled for 48 h and sintered in the temperature interval from 1000°C to 1200°C exhibit a water absorption of less than 0.5%. A high hardness of 2 – 5.82 GPa was obtained for the samples milled for 12 h, 24 h, and 48 h. The water absorption and hardness of the sintered samples achieve the standar's requirement for unglazed clay ceramic tiles. The result of water adsorption and hardness suggest that it is possible to use clay and sago waste as a raw material for producing the ceramic floor tile.

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**Садржај:** Мешањем отпадног пепела из индустријске прерађивачке производње сагоа из Индонезије са глином, добијена је нова врста керамичких материјала. Додавањем 50 %wt отпада на бази сагоа у глину добијен је састав чији су узорци млевени 6, 12, 2 и 48 сати, истим редоследом.

Узорци су пресовани на суво а затим синтеровани у температурском интервалу од 800 до 1200°C. Детаљно је проучаван утицај температуре синтеровања и времена млевења на густину узорака, скупљање током синтеровања, адсорпцију воде и чврстоћу. Резултати су показали да су ниска адсорпција воде, мања од 0,5%, и велика чврстоћа од 5,82 GPa, постигнута за узорке синтероване на 1100°C и млене 48 сати. Проучавање адсорпције ових керамика указују на то да би их требало користити као материјале за производњу неглазираних подних плочица.

**Кључне речи:** неглазирана подна плочица, отпад сагоа, глина, температура синтеровања, време млевења, адсорпција воде, чврстоћа.

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